

**TUNABLE FAR INFRARED STUDIES OF MOLECULAR PARAMETERS  
IN SUPPORT OF STRATOSPHERIC MEASUREMENTS**

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**Annual Report  
Progress Through December 31, 1995**

**NASA Grant NAGW-1292  
Tunable Far Infrared Studies in Support of Stratospheric Measurements**

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**Introduction**

This report summarizes research done under NASA Grant NAGW-1292 through December 31, 1995. The research performed during this reporting period includes spectroscopic studies to determine molecular parameters from OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, and HI.

We have now developed an expertise in ultra-high resolution spectroscopy using the TuFIR method that includes:

- The development of radical source chemistries, allowing us to measure pressure broadening and line positions of OH, HO<sub>2</sub> and ClO;
- Development of 3-wave mixing, which trades off some of the power available in the tunable far infrared beam for much wider tunability. For a particular measurement, either 2-wave or 3-wave mixing can be chosen according to experimental need;
- Design and fabrication of spectroscopy cells, a flow-metering system for radical chemistry, and other laboratory apparatus;

- Development of instrument control and data acquisition software, allowing for precise control of the TuFIR instrument parameters and long integration times for weak spectral lines and;
- Development of software for nonlinear least-squares fitting of measured spectra to obtain pressure broadening coefficients and/or line positions, based upon the algorithm of Marquardt [5]. Spectra which have the typical modulation-broadened Voigt derivative line shape (other line shape options are available as well, including normal Voigt and Voigt second derivative) are calculated using a complete radiative transfer model, including the effects of line saturation and modulation broadening. Voigt line profiles and their derivatives are calculated, with the capability of varying Doppler and Lorentz widths, line positions, absorber amounts, and baseline and laser power curve variations modeled with polynomials up to cubic order.
- Development of software to perform multiple linear regressions to obtained line broadening and/or shifting information from studies employing complex source chemistries.
- Development of Hamiltonian fitting capability that includes asymmetric top molecules with centrifugal distortion up to octic, with electron spin, nuclear spin, and nuclear quadrupole interactions.

Thus we are in a very good position for continuing with our ongoing program of far infrared line parameter measurements. In particular, we have developed a capability for performing these measurements on radical species and on weak lines that is unique.

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